High order WKB prediction of the energy splitting in the symmetric double well potential

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The accuracy of the WKB approximation when predicting the energy splitting of bound states in a double well potential is the main subject of this paper. The splitting of almost degenerate energy levels below the top of the barrier results from the tunneling and is thus supposed to be exponentially small. By using the standard WKB quantization we deduce an analytical formula for the energy splitting, which is the usual Landau formula with additional quantum corrections. We also examine the accuracy of our and Landau formula numerically for the case of the symmetric double well quartic potential.

§1. Introduction

Apart from the perturbative and variational methods the semiclassical or WKB approximation is the most widely used approximation in quantum mechanics to obtain the analytic expressions. The semiclassics serves not only as an approximative tool but it also helps us to picture and to understand the global behaviour of eigenfunctions and energy spectra of quantum systems which is particularly important in the context of quantum chaos [1), 2)]. Since the systematic study of the accuracy of semiclassical approximation is a difficult task, it has been attempted for simple systems, where in a few cases even exact solutions may be worked out [3), 4), 5), 6), 7)].

In this paper we analyze the energy splitting of doublets in a generic one–dimensional double well potential. The splitting due to the tunneling is supposed to be exponentially small and is thus lost a-priori in the semiclassical approximation by expanding the quantum phase in the $\hbar$ power series. By using the standard WKB technique we deduce an analytical formula for the energy splitting which is the usual Landau [8)] formula with additional quantum corrections and can be formally written as

$$\Delta E = A \exp\left[-\frac{S}{\hbar}\right], \qquad (1\cdot1)$$

where S is the usual classical action inside the classically forbidden region (between the two turning points) and A is called the tunneling amplitude, which can be written as an $\hbar$ power series. This formula is based on a linear approximation of the potential near the turning points and so is inapplicable in the case of the square potentials [9)].

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First we introduce the basic definitions, then we present the WKB splitting formula based on the higher order semiclassical WKB expansion and finally we study its validity for the quartic potential. We shall demonstrate that our formula is indeed a significant improvement of the Landau approximation [8]. Also, we shall mention some potential applications in the field of molecular physics.

§2. Basic formalism

Let us consider a particle in a one–dimensional symmetric double–well potential. The stationary Schrödinger equation of the system reads as

$$\hat{H}\psi(x) = \Big(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\Big)\psi(x) = E\psi(x)\,. \qquad (2\cdot1)$$

The Sturm–Liouville theorem (see, for example [10]) ensures that for one–dimensional systems there are no degeneracies in the spectrum. Let ψ_1 and ψ_2 be two exact and almost degenerate eigenfunctions of the Schrödinger equation corresponding to the energy eigenvalues E_1 and E_2 lying below the top of the barrier. We write the eigenfunctions ψ_1 and ψ_2 in terms of the right and left localized functions

$$\psi_0(x) = \frac{1}{\sqrt{2}}(\psi_1(x) + \psi_2(x)) \qquad \text{and} \qquad \psi_0(-x) = \frac{1}{\sqrt{2}}(\psi_1(x) - \psi_2(x))\,. \quad (2\cdot2)$$

It is easy to show that $E_0 =< \psi_0(x)|\hat{H}|\psi_0(x) >=< \psi_0(-x)|\hat{H}|\psi_0(-x) >= \frac{1}{2}(E_1 + E_2)$ and

$$\Delta E = E_2 - E_1 = \frac{2\hbar^2}{m}\psi_0(0)\psi'_0(0)\,, \qquad (2\cdot3)$$

(see [8), 9)]). We shall remark that so far this is an almost exact starting formula to calculate the energy splitting, since the error committed in the derivation is only exponentially small [8), 9)]. Please note that this quantity is always positive, because the tail of the right localized eigenfunction $\psi_0(x)$ at $x = 0$ has the same sign for $\psi_0(0)$ and its derivative $\psi'_0(0)$.

§3. Semiclassical method

The WKB splitting formula is obtained by inserting the WKB approximant for the right localized function ψ_0 which is determined by the WKB expansion of the Schrödinger equation [11]. A generic eigenfunction ψ of the Schrödinger equation can always be written as

$$\psi(x) = \exp\Big(\frac{i}{\hbar}\sigma(x)\Big)\,, \qquad (3\cdot1)$$

where the phase $\sigma(x)$ is a complex function that satisfies the Riccati differential equation

$$\sigma'^2(x) + (\frac{\hbar}{i})\sigma''(x) = 2m(E - V(x))\,. \qquad (3\cdot2)$$

The WKB expansion for the phase is given by

$$\sigma(x) = \sum_{k=0}^{\infty} (\frac{\hbar}{i})^k \sigma_k(x)\,. \tag{3·3}$$

Substituting (3·3) into (3·2) and comparing like powers of $\hbar$ gives the recursion relation $(n > 0)$ [3)]

$$\sigma'^2_0 = 2m(E - V(x))\,, \quad \sum_{k=0}^{n} \sigma'_k \sigma'_{n-k} + \sigma''_{n-1} = 0\,. \tag{3·4}$$

The first five orders in the WKB expansion are given in the Appendix.

In particular, if we call a and b the two turning points (let $a < b$) corresponding to the energy E, the right localized wavefunction ψ_0 for the forbidden region $x < a$ that enters the splitting formula is given by

$$\psi_0(x) = \frac{C}{\sqrt{|\tilde{p}|}} \exp\left[\frac{1}{\hbar}\left(\int_a^x |\tilde{p}|\,dx + \tilde{\sigma}_{even} + \tilde{\sigma}_{odd}\right)\right]\,, \tag{3·5}$$

where

$$\tilde{\sigma}_{even} = \sum_{k=1}^{\infty} \hbar^{2k} \underline{\tilde{\sigma}_{2k}}(|\tilde{p}(x)|); \quad \tilde{\sigma}_{2k}(x) = \underline{\tilde{\sigma}_{2k}}(|\tilde{p}(x)|) = \int_a^x \underline{\tilde{\sigma}'_{2k}}(|\tilde{p}(\xi)|)d\,\xi\,, \tag{3·6}$$

$$\text{with} \quad \underline{\tilde{\sigma}_{2k}}(-|\tilde{p}|) = -\underline{\tilde{\sigma}_{2k}}(|\tilde{p}|)\,,$$

and

$$\tilde{\sigma}_{odd} = \sum_{k=1}^{\infty} \hbar^{2k+1} \underline{\tilde{\sigma}_{2k+1}}(|\tilde{p}(x)|); \quad \tilde{\sigma}_{2k+1}(x) = \underline{\tilde{\sigma}_{2k+1}}(|\tilde{p}(x)|) = \int^x \underline{\tilde{\sigma}'_{2k+1}}(|\tilde{p}(\xi)|)d\,\xi \tag{3·7}$$

$$\text{with} \quad \underline{\tilde{\sigma}'_{2k+1}}(-|\tilde{p}|) = \underline{\tilde{\sigma}'_{2k+1}}(|\tilde{p}|)\,,$$

where $\tilde{p} = \sqrt{2m(V(x) - E)}$ and if we define $\sigma'_k(x) = \underline{\sigma'_k}(p(x)) = f_k(p(x))$ then $\tilde{\sigma}'_k(x) = \underline{\tilde{\sigma}'_k}(\tilde{p}(x)) = f_k(\tilde{p}(x))$, for f_k being the same function of an appropriate argument in both cases and $\underline{\tilde{\sigma}_k}(|\tilde{p}(x)|)$ is considered as a family of functionals. In evaluating the integrals σ_k and $\tilde{\sigma}_k$ we cannot integrate naively on the real axis, because such integrals are divergent, but must take a partial derivative w.r.t. the energy of certain fundamental complex contour integral [3)]. For potentials with only one minimum, thus having only two turning points, this has been proven by Robnik and Romanovski [13)].

The constant C is determined by the Kramers correspondence formula [12)] and normalization condition for the right localized function

$$1 = \int_0^{\infty} |\psi_0(x)|^2 dx\,, \tag{3·8}$$

which reads as

$$2C^2 \int_a^b \frac{1}{p} \exp\left(2\frac{\sigma_{odd}}{\hbar}\right) dx = 1\,, \tag{3·9}$$

that is approximately an integral of the semiclassical probability density $|\psi_0(x)|^2$ over the classically allowed region $a < x < b$ [9].

In this way the splitting formula, up to the 5th order, after taking into account straightforward recursion relation (3·4) for σ_k' or $\tilde{\sigma}_k'$ becomes

$$\Delta E = \frac{\hbar}{m}\left[\int_a^b \frac{1}{p}\,dx\right]^{-1} \exp\left[-\frac{2}{\hbar}\int_0^a |\tilde{p}|\,dx\right]\left\{1 + 2\hbar\tilde{\sigma}_2(0) + 2\hbar^2\left(\tilde{\sigma}_2^2(0) + \frac{\int_a^b \frac{\sigma_3}{p}\,dx}{\int_a^b \frac{1}{p}\,dx}\right)\right.$$
$$+2\hbar^3\left(\tilde{\sigma}_4(0) + \frac{2}{3}\tilde{\sigma}_2^3(0) + 2\tilde{\sigma}_2(0)\frac{\int_a^b \frac{\sigma_3}{p}\,dx}{\int_a^b \frac{1}{p}\,dx}\right) + 2\hbar^4\left(\frac{1}{3}\tilde{\sigma}_2^4(0) + 2\tilde{\sigma}_2(0)\tilde{\sigma}_4(0)\right)$$
$$\left. + 2\hbar^4\left(2\tilde{\sigma}_2^2(0)\left[\frac{\int_a^b \frac{\sigma_3}{p}\,dx}{\int_a^b \frac{1}{p}\,dx}\right] + 2\left[\frac{\int_a^b \frac{\sigma_3}{p}\,dx}{\int_a^b \frac{1}{p}\,dx}\right]^2 - \frac{\int_a^b \frac{\sigma_3^2+\sigma_5}{p}\,dx}{\int_a^b \frac{1}{p}\,dx}\right)\right\} \qquad (3\cdot10)$$

This formula is the usual Landau [8] formula for the energy splitting (1st order in $\hbar$ for the tunneling amplitude) with additional quantum corrections (up to the 5th order in $\hbar$ for the tunneling amplitude). We note that higher–order WKB corrections quickly increase in complexity [5), 6)] but, in principle, they can be calculated from the equation (3·4). It is important to stress that our splitting formula is good if the potential is sufficiently smooth so that the linear approximation and so the Kramers correspondence relations are valid near the turning points.

The same splitting formula (3·10) can be derived using the semiclassical scattering formalism and Kramer correspondence rules, for example as expounded by Iyer and Will [14] and by Will and Guinn [15]. However, it is necessary to go back to the very first step in their formalism to get the result (3·10) of our problem. We have done this and confirmed, as mentioned above, that the result is the same.

§4. Quartic potential

As one of our test models we consider the symmetric double well quartic potential, given by

$$V(x) = -2Bx^2 + Ax^4\,, \qquad (4\cdot1)$$

where the parameters A and B are related to the potential barrier V_0 and to the position of the minimum x_0 by

$$V_0 = \frac{B^2}{A}, \quad x_0 = \sqrt{\frac{B}{A}}\,. \qquad (4\cdot2)$$

By using the following reduced variables

$$\bar{x} = \frac{x}{x_0}\,, \quad \bar{E} = \frac{E}{V_0}\,, \quad \hbar_{eff} = \frac{\hbar}{x_0\sqrt{mV_0}}\,, \qquad (4\cdot3)$$

the quantum Hamiltonian operator of the system can be written as

$$\hat{H} = -\frac{\hbar_{eff}^2}{2}\frac{\partial^2}{\partial\bar{x}^2} - 2\bar{x}^2 + \bar{x}^4\,. \qquad (4\cdot4)$$

The exact spectrum of operator (4·4) is calculated by numerical diagonalization of the Hamiltonian matrix, written in the basis of harmonic oscillator in QUADRUPLE PRECISION number format (32 digits) [9].

The quantities $\tilde{\sigma}_0(0)$, $\tilde{\sigma}_2(0)$, $\tilde{\sigma}_4(0)$, $\int_a^b \frac{1}{p}\,dx$, $\int_a^b \frac{\sigma_3}{p}\,dx$ and $\int_a^b \frac{\sigma_3^2+\sigma_5}{p}\,dx$ that enters the semiclassical splitting formula can all be expressed in terms of complete elliptic integrals of the first and the second kind [9].

Please note that all the integrands of these quantities are strongly divergent at the turning points, but all the expressions in (3·10) can be made convergent and finite by taking partial derivatives with respect to E of certain finite expressions [3), 5), 6), 9)].

In figure 1 we show the tunneling amplitude A as a function of the mean energy $\bar{E}$ of all almost degenerate pairs of quartic potential with $\hbar_{eff} = 0.03$. We compare the exact results with the semiclassical ones at 1st (Landau), 3rd and 5th order in $\hbar$. We can observe that, as expected, the agreement is better at the energies for which the well known semiclassical criterion is fulfilled. The criterion demands the absolute value of the de Broglie wavelength to be small compared to the typical scale of the potential. This is not the case at energies near the top and at the bottom of the potential barrier but the accuracy increases when going with the energy away from those two values. In figure 2 (3) we plot the tunneling amplitude A as a function $\hbar_{eff}$ for the first (fourth) pair of almost degenerate consecutive energy levels. As shown also in table 1, the semiclassical results approach the exact ones by increasing the perturbative order in $\hbar$. Note that at the 5th order in $\hbar$ the agreement with exact result is up to the 8th digit.

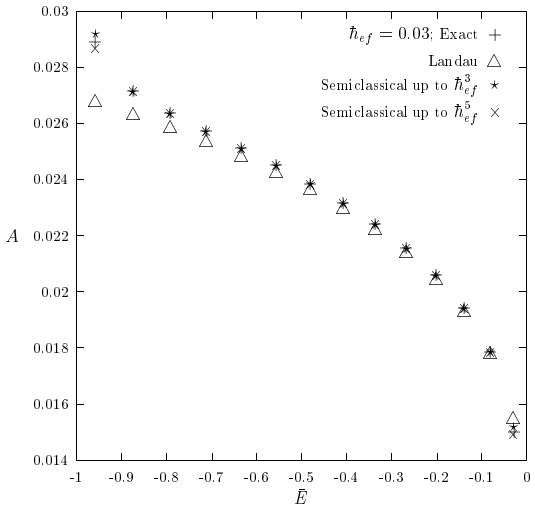

Fig. 1. Tunneling amplitude A *vs* mean energy $\bar{E}$ of Quartic potential with $\hbar_{eff} = 0.03$.

§5. Conclusions

In this work we have taken the first step towards a systematic improvement of the Landau formula [8], which is the semiclassical leading order energy level splitting formula for pairs of almost degenerate levels in double well potentials. We have developed the algorithm for the semiclassical $\hbar$ expansion series to all orders for the tunneling amplitude A (of equation (1·1)), and thus calculated explicitly the quantum corrections up to the 5th order. We have compared the semiclassical predictions with the exact results obtained numerically, for the case of the quartic double well potential. Our approach is based on the usual WKB expansion in one–dimensional

potentials and so the calculation of higher corrections can in principle be continued by the same method, although the structure of higher terms increases in complexity very quickly. We have also checked what happens in cases where the assumption implicit in the Landau formula (namely the linearity of the potential around the turning points) is not satisfied as in the case of double square well potential: We get a different result even in the leading semiclassical order [9]. We should stress that the Landau formula [8] is indeed quite good approximation since it always yields the correct order of magnitude (the exponential tunneling factor is always correct) and even the tunneling amplitude is correct within the 5–50 % .

It is our goal to work out a more direct WKB approach to the solution of the multi–minima problem, by the contour integration technique, based on requiring the single valuedness of the eigenfunction, as has been done by Robnik and Salasnich [5), 6)] in the case of a single well potential. This is our future project.

Finally we should mention important applications e.g. in the domain of molecular physics [8), 16), 17)]. For example, the NH_3 molecule can be described by a quasi one-dimensional potential $V(x)$ as a function of the perpendicular distance x of the nitrogen N atom from the H_3 plane, and as such it has the double well form, with the top of the potential barrier at $x = 0$. In order to calculate the energy level splitting of the doublets of vibrational modes one needs exactly our theory. Another example is the torsional motion of C_2H_4 molecule, where again we encounter an effectively one-dimensional double well potential. In case of C_2H_6 molecule, we find three potential wells where the tunneling effects again determine the splittings of energy triplet levels and a generalization of our theory would give an improved estimate of the splittings.

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Appendix

The first 5 orders in the WKB expansion are:

$$\sigma_0' = p\,,$$

$$\sigma_1' = -\frac{p'}{2p}\,,$$

$$\sigma_2' = \frac{p''}{4p^2} - \frac{3}{8}\frac{p'^2}{p^3}\,,$$

$$\sigma_3' = \frac{p'''}{8p^3} + \frac{3}{4}\frac{p'p''}{p^4} - \frac{3}{4}\frac{p'^3}{p^5}\,,$$

$$\sigma_4' = \frac{1}{16}\left(\frac{p''''}{p^4} - 10\frac{p'''p'}{p^5} - \frac{13}{2}\frac{p''^2}{p^5} + \frac{99}{2}\frac{p''p'^2}{p^6} - \frac{297}{8}\frac{p'^4}{p^7}\right), \qquad (5\cdot1)$$

$$\sigma_5' = \frac{1}{32}\left(-\frac{p'''''}{p^5} + 15\frac{p''''p'}{p^6} + 24\frac{p'''p''}{p^6} - 111\frac{p'''p'^2}{p^7} - 144\frac{p''^2p'}{p^7} + 510\frac{p''p'^3}{p^8} - 306\frac{p'^5}{p^9}\right).$$

The derivatives $\tilde{\sigma}_k'$-s can be obtained by replacing $p(x)$ by $\tilde{p}(x)$ in the expressions above.

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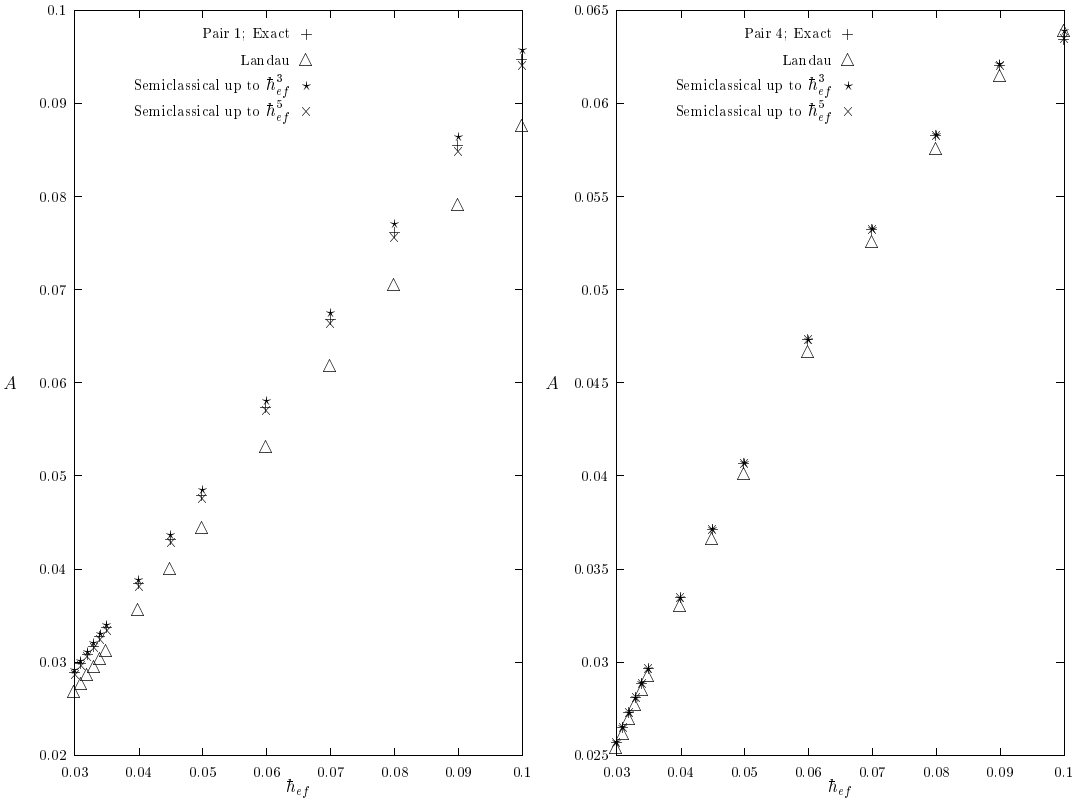

Fig. 2. Tunneling amplitude A *vs* $\hbar_{eff}$ for the first pair of almost degenerate consecutive energy levels (left). The same plot for the forth pair of almost degenerate consecutive energy levels (right). Quartic potential.

Table I. Energy splitting $\Delta\bar{E}$ for all almost degenerate pairs at $\hbar_{eff} = 0.03$. $\bar{E}_s$ is the exact mean energy, $\Delta\bar{E}_{Landau}$, $\Delta\bar{E}_{\hbar^3}$ and $\Delta\bar{E}_{\hbar^5}$ are the semiclassical results at 1st (Landau), 3rd and 5th order, respectively. In the last column of the upper table: exact energy splitting in units of mean level spacing.

Pair number	$\bar{E}_s$	$\Delta\bar{E}_{Exact}$	$\Delta\bar{E}_n/(\overline{\bar{E}_s^{n+1} - \bar{E}_s^n})$
1	-0.9578013510838623	9.232(2)E-28	1.291(6)E-26
2	-0.8743363182686136	6.533698E-25	9.140541E-24
3	-0.7923227236203907	2.197647599E-22	3.074474586E-21
4	-0.7118393444104010	4.66709587543E-20	6.52919406381E-19
5	-0.6329771419061873	7.0097983270055E-18	9.8065981172742E-17
6	-0.5558426330893027	7.901944841994295E-16	1.10546971247045E-14
7	-0.4805627052945287	6.920784581323967E-14	9.68206928062435E-13
8	-0.4072917698084478	4.806630946488390E-12	6.72440144371474E-11
9	-0.3362229365299848	2.675674688376366E-10	3.74322699989559E-09
10	-0.2676066496781732	1.196767019706533E-08	1.67425832453064E-07
11	-0.2017846855780184	4.273586943459416E-07	5.97868122857108E-06
12	-0.1392610433553887	1.195177462312803E-05	1.67203455862220E-04
13	-8.088844930248588E-02	2.500127371158503E-04	3.49763905139656E-03
14	-2.855578436131249E-02	3.352190557610379E-03	4.68966210972998E-02

$\Delta\bar{E}_{Landau}(\bar{E}_s)$	$\Delta\bar{E}_{\hbar^3}(\bar{E}_s)$	$\Delta\bar{E}_{\hbar^5}(\bar{E}_s)$
8.56386072023299E-28	9.**3**3424576483334E-28	9.1**6**991849898935E-28
6.**3**4511775769322E-25	6.53**7**96204696428E-25	6.533**3**2080224002E-25
2.1**5**758453279967E-22	2.197**9**8578660872E-22	2.1976**3**766003663E-22
4.6**0**423712282166E-20	4.667**3**7049838592E-20	4.66709**2**38092202E-20
6.9**3**436277656352E-18	7.010**0**0176474235E-18	7.00979**7**08264343E-18
7.8**3**077639810467E-16	7.902**0**7840692513E-16	7.901944**4**5833250E-16
6.8**6**703907509728E-14	6.9208**6**233123417E-14	6.9207845**1**430764E-14
4.7**7**381431395796E-12	4.8066**7**193943203E-12	4.806630**8**878842E-12
2.6**5**943820818162E-10	2.6756**9**528644699E-10	2.675674**7**543535E-10
1.19**0**31027734624E-08	1.1967**7**788146677E-08	1.196767**1**4995564E-08
4.2**5**3535592752249E-07	4.2736**5**612082292E-07	4.27358**9**20983707E-07
1.19**0**79278916304E-05	1.1952**4**083756918E-05	1.19518**3**71126262E-05
2.49**8**35207740361E-04	2.50**1**42635772383E-04	2.500**5**8564705645E-04
3.4**6**270869995442E-03	3.3**9**489990444765E-03	3.3**3**278741702504E-03